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OXIDATION RESISTANCE OF SILICON CERAMICS

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16. Abstract

The article provides a review with eight references on the oxidation resistance, and examples of oxidation of SiC, Si_3N_4 and sialon. A description is given of the oxidation mechanism, including the oxidation product, oxidation reaction and the bubble size. The oxidation reactions are represented graphically. An assessment is made of the oxidation process, and an oxidation example of silicon ceramics is given.

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OXIDATION RESISTANCE OF SILICON CERAMICS

Hasegawa Yasutoshi and Kazushi Hirota[**]

1. PREFACE

The development of scientific technology demands increasingly high standards for basic materials. Fire-resistant materials composed mainly of metallic oxides have been used widely in various high-temperature industries. Recent research has focussed on nitride, carbide, silicide and boride as a fire-resistant material. Much research has been done especially on nitride, carbide and acid nitride as high-temperature-resistant structural materials. From the energy conservation perspective, these materials are expected to be improved. These materials possess superior characteristics that other oxidized substances do not have. However, they tend to oxidize easily in a high-temperature environment. Unless a solution to this problem characteristic of the materials can be found, the economical use of these materials as a pyrogenic heat-resistant structural material in an oxidizing environment cannot be realized. Among the substances that are being discussed, Si_3N_4, SiC and sialon are the first to be used as a superior fire-resistant material or partial heat-resistant structural material because of their relatively cheap prices and comparatively high purity. Their defects caused by oxidation during their usage, however, are the major obstacles hindering their further improvement. In this article, Si_3N_4, SiC and sialon are all considered as silicon ceramics and their oxidation process at a high temperature is discussed.

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[*] Numbers in margin indicate foreign pagination.

[**] (National Institute for Research in Inorganic Materials);
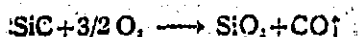On the Oxidation Properties of Silicon Ceramics

2. OXIDATION MECHANISM

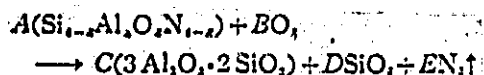(a) The oxidation of Si_3N_4 proceeds in a reaction as indicated below.

$$Si_3N_4 + 3 O_2 \longrightarrow 3 SiO_2 + 2 N_2 \uparrow$$
$$Si_3N_4 + O_2 \longrightarrow Si_2ON_2 + SiO \uparrow + N_2 \uparrow$$
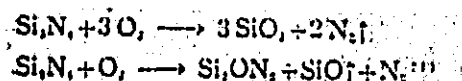
(b) Similarly, oxidation of SiC takes place as follows:

$$SiC + 3/2 O_2 \longrightarrow SiO_2 + CO \uparrow$$

(c) Sialon's oxidation goes through the following reaction.

$$A(Si_{1-x}Al_xO_xN_{1-x}) + BO_2$$
$$\longrightarrow C(3 Al_2O_3 \cdot 2 SiO_2) + DSiO_2 + EN_2 \uparrow$$
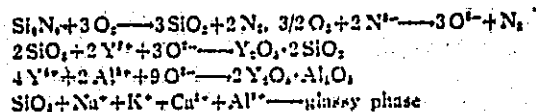
As shown in the above formulas, all of the materials increase in weight as the reaction proceeds. Generally, weight increase is the basis for an oxidation resistance assessment which will be discussed in detail in the following chapter. To give an example, sintered Si_3N_4's (Y_2O_3 and Al_2O are added as sintering auxiliary agents) oxidation process is shown in Figure 1. An analysis on the surface oxidation product by X-ray diffraction indicates that the strength of crystalline barite increases drastically at an early stage of oxidation, but as oxidation progresses, the strength decreases. After many hours of oxidation, the strength of crystalline barite drops to a point when it is no longer measurable. In inverse proportion to decreasing strength of crystalline barite, the glassy phase increases its strength. Y_2O_3 that was added as sintering agent together with Al_2O_3 reacts to SiO_2 which is produced by oxidation and forms $Y_2O_3 \cdot 2SiO_2$ with gradually increasing strength. Similarly, after a long period of oxidation, Al_2O_3 can be found in the form $2Y_2O_3 \cdot Al_2O_3$. These oxidation product actions are easy to understand when you look at them as surface accumulations of impurities in a sinter by pyrogenic oxidation.

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Figure 1. Oxidation reaction and oxidation chart of pressurized sinter Si_3N_4 (sintering agent, Y_2O_3); 5, Al_2O_3: 3 wt %)
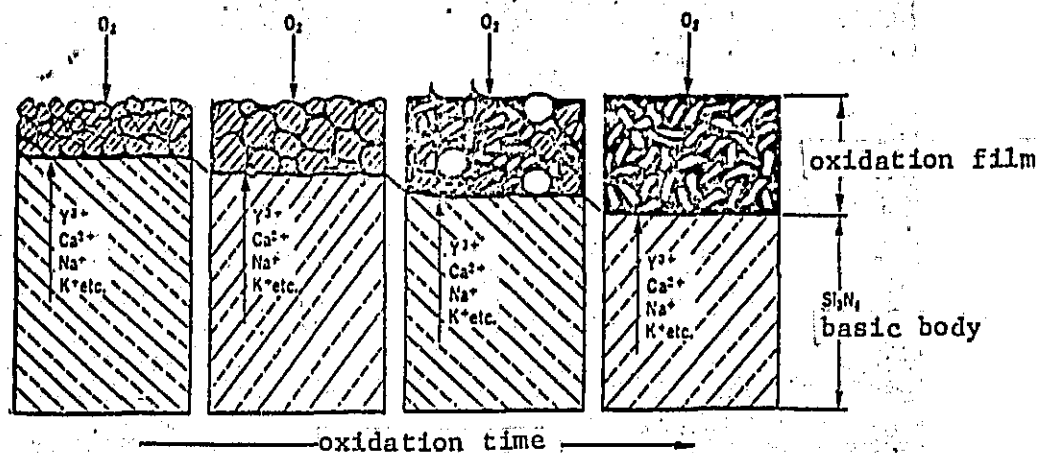
1) Oxidation product (comparison of intensity of diffracted X-ray) crystalline barite < crystalline barite > crystalline barite > N.D.

$$Y2S < Y2S < Y2S < Y2S$$
$$N.D. \quad N.D. \quad N.D. \quad (2YA)$$

sinter < sinter < sinter < sinter

2) Oxidation reaction

$$Si_3N_4 + 3O_2 \longrightarrow 3SiO_2 + 2N_2, \quad 3/2O_2 + 2N^{3-} \longrightarrow 3O^{2-} + N_2$$
$$2SiO_2 + 2Y^{3+} + 3O^{2-} \longrightarrow Y_2O_3 \cdot 2SiO_2$$
$$4Y^{3+} + 2Al^{3+} + 9O^{2-} \longrightarrow 2Y_2O_3 \cdot Al_2O_3$$
$$SiO_2 + Na^+ + K^+ + Ca^{2+} + Al^{3+} \longrightarrow glassy \; phase$$

3) Bubble size (µm) (AME sample, 1300°C oxidation):
— 10-30   200-500

In a similar manner, Figure 2 shows the oxidation process of pressurized Si_3N_4 sinter. (Sinter agent, MgO: 5 wt % added). A scanning electron microscope shows an aggregate of crystals in the post oxidation surface, which looks like a porous oxidation film. However, further analysis of the section by a scanning electron microscope and an optical microscope reveal that the closer the oxidation layer gets to the surface, the more porous it gets. The part of the layer close to the basis is very fine. This is because impurities in the base accumulate on the surface during the oxidation process, forming a layer of fine glassy phase near the base and a porous layer as it goes to the top due to the on-going crystalization process [3].

3

top layer (porous)

middle layer (relatively fine)

bottom layer (fine)

base Si_3N

$Si_3N_4+3O_2=3SiO_2+2N_2$

SiO_2—crystalline barite

$1/2 O_2+N^{3-}\longrightarrow O^{2-}+1/2 N_2$

$1/3 Si_3N_4+Mg^{2+}+3O^{2-}\longrightarrow MgSiO_3+4/3 N^{3-}$

$2/3 Si_3N_4+Mg^{2+}+2Ca^{2+}+7O^{2-}\longrightarrow MgO\cdot 2CaO\cdot 2SiO_2+8/3 N^{3-}$

$2/3 Si_3N_4+Mg^{2+}+Ca^{2+}+6O^{2-}\longrightarrow CaO\cdot MgO\cdot 2SiO_2+8/3 N^{3-}$
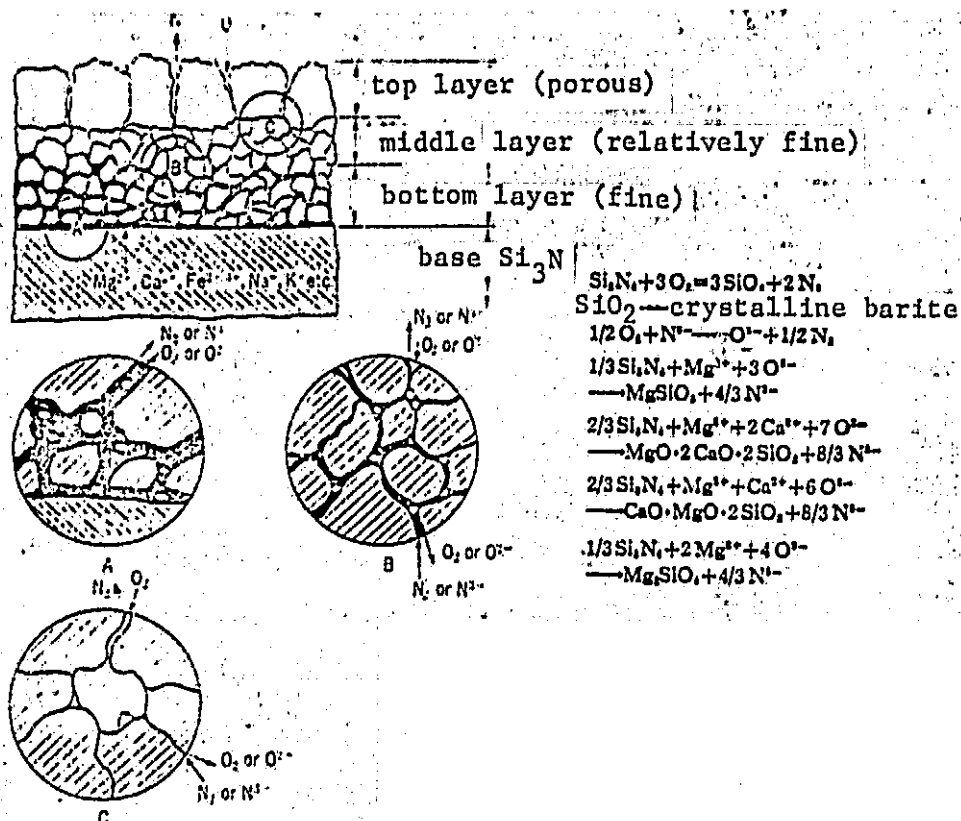
$1/3 Si_3N_4+2Mg^{2+}+4O^{2-}\longrightarrow Mg_2SiO_4+4/3 N^{3-}$

Figure 2. Oxidation reaction and chart of Si_3N_4 pressurized sinter (sinter agent MgO): 5 wt % added, 1300°C, 30d)

oxidation film

sialon (z=1-4) base

1) Oxidation weight increase

2) Oxidation film thickness

3) Oxidation products (comparison of intensity of diffracted X)

4) Oxidation reaction

5) Bubble size (μm)

$\beta_1 > \beta_2 > \beta_3 > \beta_4$

$\beta_1 < \beta_2 < \beta_3 < \beta_4$

c.b. > c.b. > c.b. > N.D.

$Si_3N_4+3O_2\longrightarrow 3SiO_2+2N_2$, $3/2 O_2+2N^{3-}\longrightarrow 3O^{2-}+N_2$

$2SiO_2+6Al^{3+}+3O^{2-}\longrightarrow 3Al_2O_3\cdot 2SiO_2$
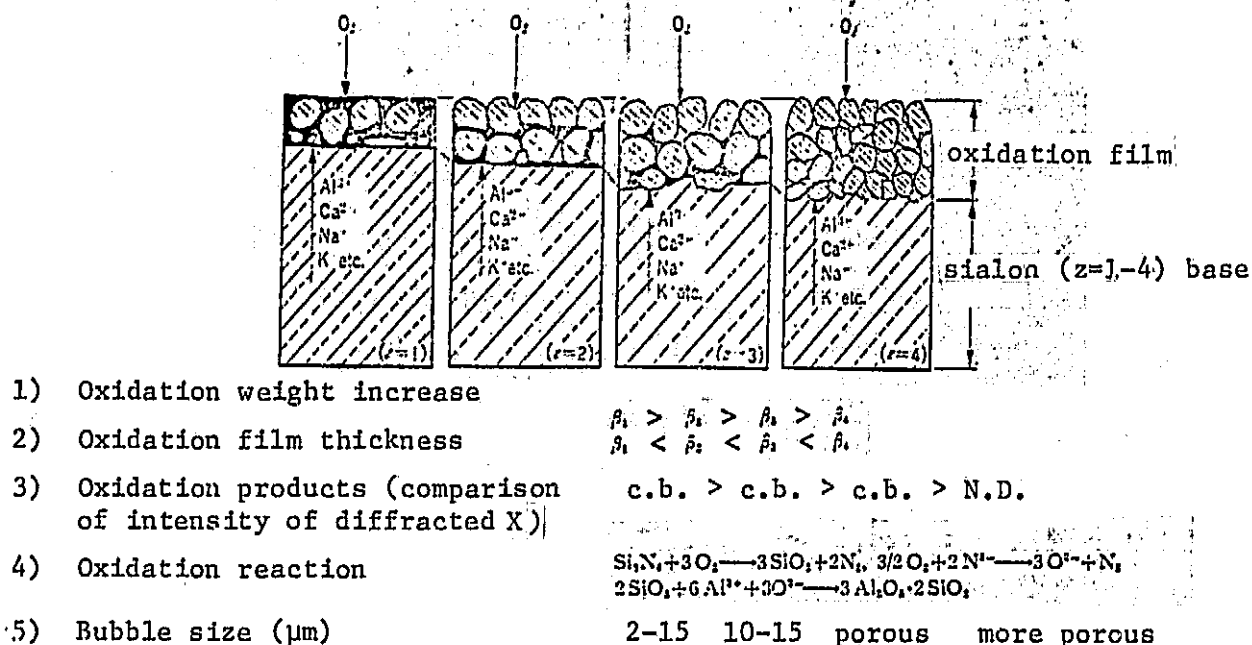
2-15   10-15   porous   more porous

Figure 3. β-sialon pressurized sinter oxidation reaction (z=1-4) and chart (1300°C, 30d)   [2]

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Figure 3 shows oxidation of sialon which sinters relatively easily without an agent (can be considered as a single phase). An oxidation experiment with sialon sinter offered an interesting result: from Z=1 to Z=4, the oxidation weight increase becomes smaller as the number goes up, whereas the thickness of the film increases as the number goes up [2]. The one with the smallest oxidation weight increase, in this case sialon Z=4, is believed to possess the best oxidation resistance. But in the case of sialon, Z-4 type composition does not necessarily have better oxidation resistance. From the point of oxidation film thickness, the Z=1 type composition is considered to have better oxidation resistance. This experimental finding demands a basic re-analysis of conventional oxidation resistance, namely the assessment based on oxidation weight increase. Based upon a study of the oxidation mechanism of SiC, SiC sinter forms crystalline barite on the surface while a part of sinter agents (normally B, C and Al) accumulate on the surface as well, in the same way as Si_3N_4 sinter which is indicated in Figure 1. B oxidizes easily and evaporates as B_2O_3 at or above 1300°C. As an example, the oxidation weight increase process with B: 0.5 w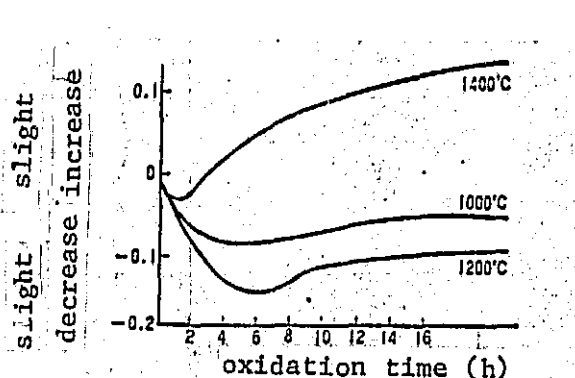t % and Al: 1 wt % added is shown in Figure 4. Considering the above discussion, silicon ceramic oxidation may seem simple, but in actuality, it is quite a complicated process.

Figure 4. Pressurized sinter SiC (B oxidation mechanism [5]. (B: 0.5 wt %, AL: 1.0 wt %)

3. ASSESSMENT STANDARD OF OXIDATION PROCESS

In the previous chapter, it was pointed out that the conventional oxidation resistance assessment by means of the

oxidation weight increase entails problems. As assessment
criteria of oxidation resistance, aside from weight increase,
one may consider the thicknesses of the oxidation film, oxida-
tion product and the nature of oxidation film surface and bubbles.
When the primary component of oxidation products is crystalline
barite alone, oxidation film exfoliates when it cools down to
room temperature, because the crystalline barite $a \overset{\rightarrow}{\underset{\leftarrow}{}} b$ transition
takes place around 27°C. When the coefficient of thermal expan-
sion of an oxidation product differs substantially from that of
the base, shear strain occurs on the surface of contact between
the oxidation film and the base, which causes exfoliation. The
nature of the oxidation film surface is closely related to the
oxidation products. When the impurities of the base accumulate
on the surface, glass formation with a low melting point among
the impurities, causes very uneven oxidation of the film surface
due to N_2, CO gas generated by the oxidation reaction. We have
experienced a case where R_{max} reached 100 μm. As discussed, it
involves great risk to assess the overall oxidation characteristic
from one particular characteristic and it is inevitable to use a
comprehensive assessment method. To do so, we made Figure 5 by
applying the characteristic factor often used for quality control
for oxidation assessment. The factors in this figure are
insufficient; therefore, this serves as a reference of the basic
assessment method. Generally, the same oxidation experiments do
not result in accurately overlapping findings, which makes it
extremely difficult to obtain data usable as a data bank. This
is because too many factors are involved. For the assessment of
oxidation characteristics, we have to specify the characteriza-
tion of sinter, and to do so we need to characterize the original
material.

4. OXIDATION EXAMPLE OF SILICON CERAMICS

As an example, I would like to discuss Davidge and other
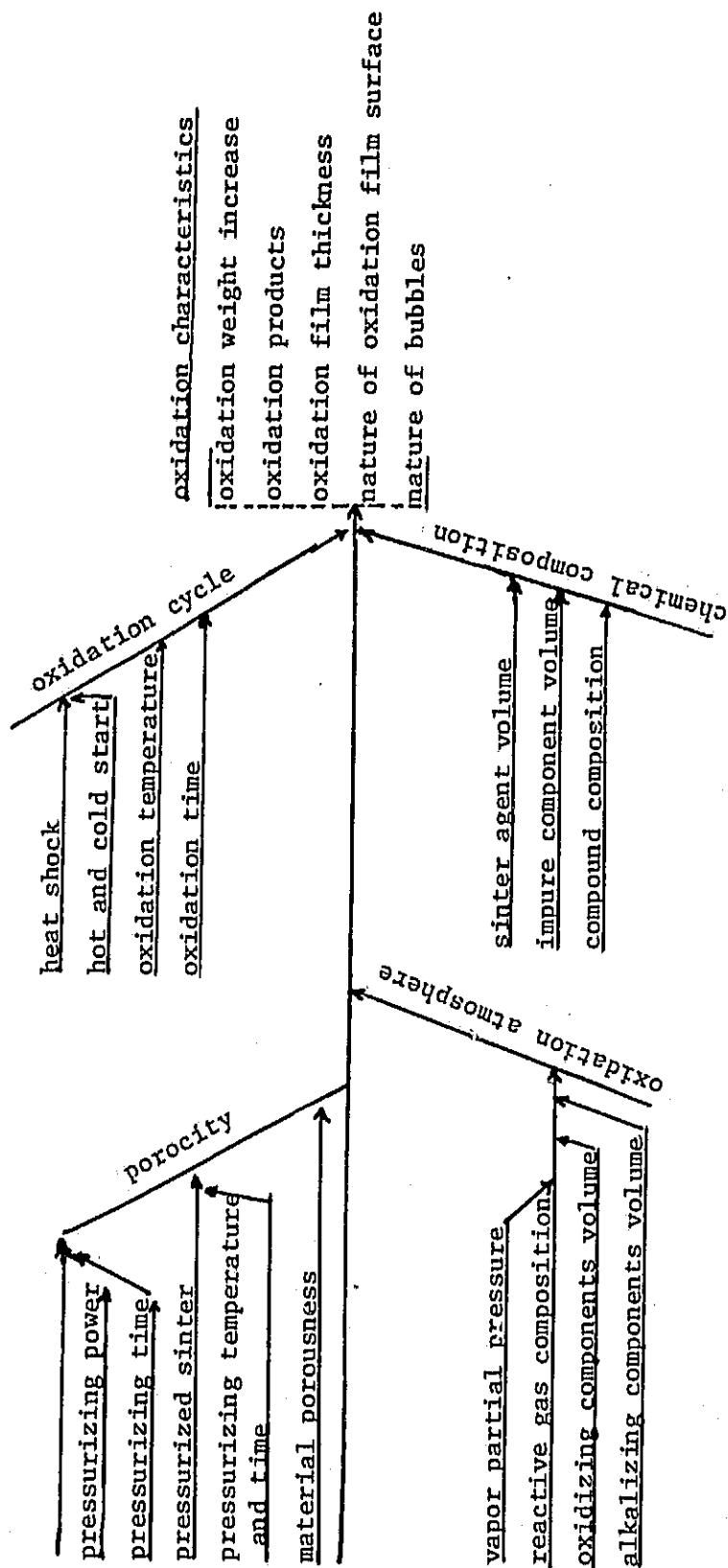experiments on reactive sinter Si_3N_4's oxidation. Organic
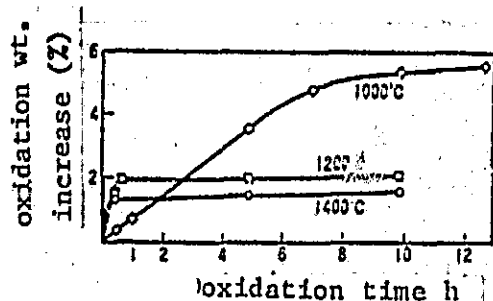
6

oxidation characteristics

oxidation weight increase
oxidation products
oxidation film thickness
nature of oxidation film surface
nature of bubbles

oxidation cycle

heat shock
hot and cold start
oxidation temperature
oxidation time

chemical composition

sinter agent volume
impure component volume
compound composition

porocity

pressurizing power
pressurizing time
pressurized sinter
pressurizing temperature and time
material porousness

oxidation atmosphere

vapor partial pressure
reactive gas composition
oxidizing components volume
alkalizing components volume

Figure 5. Characteristic factors of oxidation assessment

Figure 6. Reactive sinter Si_3N_4 oxidation weight increases in relation to oxidation time (h) [6]

binder was added to silicon powder which is available commercially. Then it was pressurized at 500 MNm^{-2}. Then nitriding was done at 1350°C for 20 hours first, followed by 20 more hours of nitriding at 1450°C, which created a test material with a density of 2.53 g/cm^3. The material was then cut into specific sizes, which was oxidized in an open furnace at three different temperatures (1000, 1200 and 1400°C) for 150 hours. Figure 6 shows the oxidation weight increase observed in the experiment.

Providing the oxidation mechanism proceeds by a simple diffusion mechanism, two clear steps of oxidation can be observed. At 1000°C, the early stage of oxidation (stage I) takes 3 to 4 days. At 1200°C or 1400°C, however, stage I is completed in about 15 minutes. Moreover, at higher temperatures, the oxidation weight increase (%) during stage I is greater, but the oxidation rate is lower. In this experiment by Davidge and others, low stages (early stage and mid-stage) of the oxidation mechanism were observed. In a series of our experiments on silicon ceramics oxidation, several stages were found as shown in Figure 7.

These stages change depending on oxidation conditions (especially oxidation atmosphere). Note that unit of oxidation time in Figure 7 is days. It has been reported that oxidation is completed primarily in stages I and II and the mechanisms can be explained as simple diffusion mechanism. However, in oxidation over a long period of time (unit = month), stages that cannot be explained by simple diffusion start to appear (stages III-IV in the figure). When there is partial steam pressure, the material reaches stages III-IV within relatively a few days.
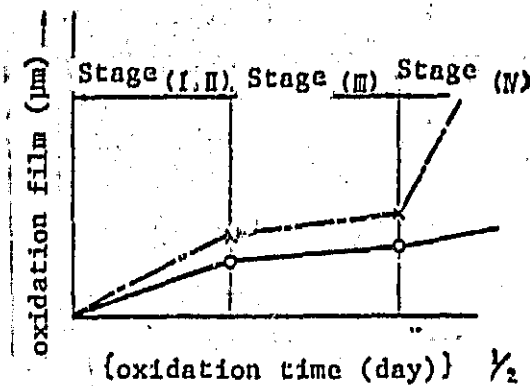
8

Figure 7. Thickness (μm) of oxidation film when oxidized at a set temperature {oxidation time (day)} $^{1/2}$
x---x   repetitive cooling and heating while maintaining the specific temperature

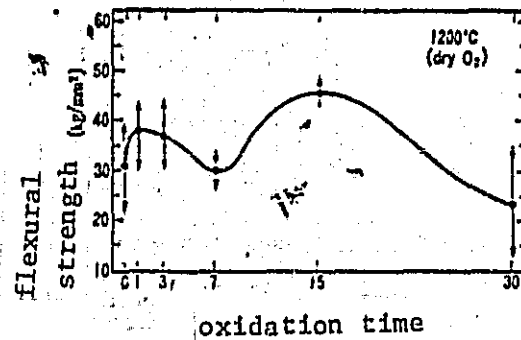o---o   keeping a general temperature steady

Figure 8. β-sialon (x=2) sinter
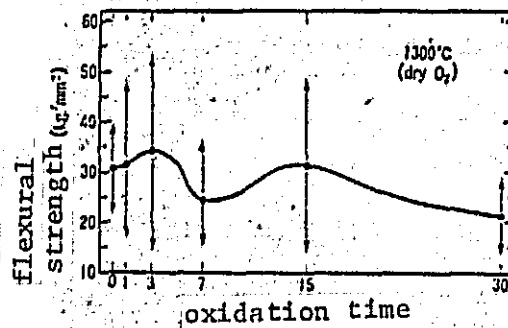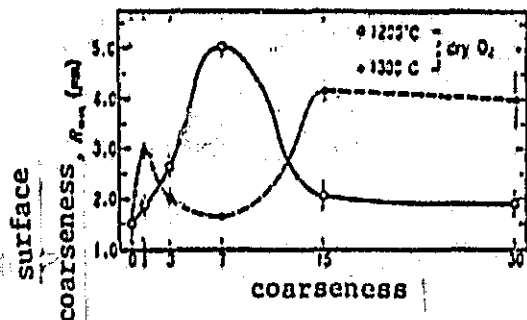

Figure 9. β-sialon (z=2) sinter

Figure 10. β-sialon (x=2) pressurized sinter surface coarseness - oxidation time

We now discuss how strength changes by oxidation. As an example, Figures 8 and 9 show data on β-sialon (z=2) pressurized sinter.

As shown in the figures, strength decreases as the oxidation time increases. At higher temperatures, the data becomes more inconsistent. It is nearly impossible to explain these phenomena in the limited number of words here, but for reference purposes, we touched upon the relation between strength and coarseness of the surface in Figure 10.

5. POSTSCRIPT

Oxidation resistance of anti-oxidizing materials depends mainly on the basic body crystals phase type, grain shape, grain distribution, grainy phase type and its distribution, porosity characteristics and distribution. Moreover, the resistance is determined mostly by physical and chemical properties of the oxidation film on the surface. Thus, accurate research on oxidation should be initiated with a study on the basic sintering process and the compound phase distribution and properties. Based upon the oxidation characteristics of the oxidation mechanism, better resistance is observed in the following conditions.

1) Oxidation weight increase: Small weight increases. Weight increases in the parabolic manner in relation to oxidation time without drastic change of pace.

2) Oxidation film thickness: Like the weight increase, the oxidation film is thin, while the thickness increases in a parabolic manner in relation to oxidation time without drastic change of pace.

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3) Oxidation product: They are non-transferable oxides. They possess a coefficient of thermal expansion similar to that of the basic body. They are not complex oxides consisting of many different components. They form fine layers.

4) Surface of oxidation film: even and smooth surface with no complicated protrusions or deflections.

A sinter with oxidation film which follows the above conditions most clearly is desirable from the viewpoint of oxidation resistance. However, an oxidation film which meets all the above conditions is not available yet. In the end, we would like to express our appreciation to Dr. Hiroshige Suzuki, honorary professor at Tokyo Kogyo University, for providing us supervision.

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Graduated from Tokyo Kogyo University, Chemical Engineering Department, in 1955 and joined Onoda Cement Co. Ltd in the same year. Since 1966, he has been working at the National Institute of Research in Inorganic Materials. He is a chief research officer and engineer of departments of chemistry, ceramics and production control, quality control. He is also a professor of engineering at Tokyo Kogyo University.

Kazushi Hirota

He graduated from Tokyo Kogyo University, Science Department, Chemistry Div. in 1957. Completed MA courses at the same university in 1959. In 1960, he became an assistant instructor at the university. In 1971, he joined the National Institute for Research in Inorganic Materials of Science and Technology Agency. Currently, he is a chief research officer of a research group, no. 15.